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Upgrading Domestic High-Iron Chromite Concentrates by Carbonyl Extraction of Excess Iron

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	min	minute
°C	degree Celsius	pct	percent
cm	centimeter	psig	pound (force) per square inch, gauge
g	gram	SLM	standard liter per minute
h	hour	wt pct	weight percent
L	liter		

UPGRADING DOMESTIC HIGH-IRON CHROMITE CONCENTRATES BY CARBONYL EXTRACTION OF EXCESS IRON

By A. Visnapuu [1] and W. M. Dressel [2]

ABSTRACT

The Bureau of Mines has upgraded high-iron domestic chromite concentrates by a carbonyl process. The upgraded chromite concentrates show as much as 10 wt pct higher Cr_2O_3 content and up to a threefold increase in the Cr:Fe ratio, compared with the starting concentrates. The high-iron chromites were first reduced to convert the iron oxides to the metal, and then treated with CO at elevated pressures and low temperatures to convert part of the metallic iron fraction to iron pentacarbonyl. Carbonylation was accelerated by the addition of H_2S in small quantities. The iron pentacarbonyl was extricated from the concentrate in the pressure reactor during carbonylation by a CO sweep through a pressure-reducing valve and passed through a decomposer at atmospheric pressure to convert it back to iron metal and CO. CO pressure, temperature, promoter trends, and other factors enhancing iron pentacarbonyl formation are presented.

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INTRODUCTION

In 1980, the metallurgical, refractory, and chemical industries in the United States consumed nearly 1 million short tons of chromite ores, yet there was no domestic mine production of this mineral during the same year. Major suppliers of chromite ores to this country, in order of decreasing tonnage, were the Republic of South Africa, the Soviet Union, the Philippines, Turkey, Albania, Finland, and Madagascar. The metallurgical industry consumed 59 pct of the chromite ores; chemical industry, 25 pct; and refractory industry, 16 pct. The average grade of chromite ores, as Cr_2O_3, used in the metallurgical, chemical, and refractory industries were 37.5 wt pct, 45.5 wt pct, and 34.8 wt pct, respectively. Further classification of the chromite ores shows that about 38 pct of the metallurgical-grade ore had a Cr:Fe ratio of 3:1 and over, 27 pct had a ratio between 2:1 and 3:1, and 35 pct had a ratio of less than 2:1 (7).[3]

While world resources of shipping-grade chromite ores are sufficient to meet conceivable demand for centuries, the bulk of this ore is concentrated in one geographic region. Over 99 pct of the estimated 36-billion-short-ton world resources are located in southern Africa, and although the rest of the world's resources are measured in millions of tons, they are small in comparison with those in Africa. Most of the U.S. chromium resources of 8 million short tons are in the Stillwater Complex in Montana and beach sands of Oregon.

Chromium has a wide range of indispensable uses for which no ready substitutes are available. In the metallurgical industry, it is used mainly for preparing stainless, full-alloy, high-strength low-alloy, and electrical steels. The refractory industry uses chromite primarily for manufacturing bricks to line metallurgical furnaces. The chemical industry consumes chromite for manufacturing sodium and potassium dichromate, which are the base materials for a wide range of chromium chemicals. Complete dependence on imported chromite ores makes the United States vulnerable to uncertain foreign sources or disrupted supply lines. To reduce this potentially serious loss or disruption of chromite ore supply, the Bureau of Mines has conducted research to beneficiate and upgrade domestic chromite ores (3, 10-11). This report presents the results of a laboratory investigation to upgrade domestic chromite concentrates by the use of carbonyl technology. Reduced chromite concentrate was reacted with CO to form volatile iron pentacarbonyl, leaving a product with increased Cr_2O_3 content and an increased Cr:Fe ratio. The carbonyl reaction is as follows:

$$Fe \cdot Cr_2O_3 + 5\ CO_{(g)} \rightarrow Cr_2O_3 + Fe(CO)_{5(g)}.$$

A number of extractive processes based on the formation of metal carbonyls have been investigated or used. High-purity nickel was produced by the Mond process for over 70 years, and more recently the Inco pressure carbonyl process was developed to permit simultaneous extraction of nickel, cobalt, and iron from mineral concentrates and metallurgical intermediates (8). Lewis (4) investigated the recovery of nickel and iron from lateritic ores. He recovered over 90 pct of the nickel and nearly 90 pct of the iron in the temperature range 110° to 130° C using small additions of NH_3 to the CO to improve recovery. Rhee (9) found best conversion at 121° C for reduced iron ore flotation tailings. Dufour-Berte and Pasero (1) used a fluidized bed reactor for reduction of iron oxide with H_2 and subsequent carbonyl formation at temperatures between 150° and 170° C and pressures between 25 and 100 atm. Okamura (6) reported 180° C as the optimum temperature for carbonylation of reduced

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

iron oxides at 200 atm and 130° C at 100 atm. Mond and Wallis (5) reported that 200° C is optimum for all pressures between 100 and 300 atm. Visnapuu (12) produced synthetic rutile from reduced ilmenite by carbonyl extraction of the iron in the ranges of 110° and 130° C and 70- to 100-atm pressure.

Common to all the carbonyl processes is the need to catalyze or promote the reaction. Sulfur or sulfur compounds have been favored for this, and without the increase in reaction rate effected by them, commercial extraction of nickel and iron as carbonyls from reduced metals probably would not be practical (8). Although the mechanism by which sulfide ions activate the metal surface and make it reactive is not precisely known, there is evidence that no more than a monolayer of the metal surface is involved. Queneau (8) reported that in amounts up to a monolayer the metal surface is composed of the metal and sulfide ions approximating the crystal habit and stoichiometry of the most stable sulfide. He proposed that activation is the result of interference with normal bonds existing on a clean metal surface, thereby producing atoms that are nearly free. In the presence of absorbed CO, such atoms form an activated metal-CO complex, which then builds up into the metal carbonyl. The surface remains uniformly active by continuously remaking the sulfide-metal bonds ruptured when metal carbonyl is removed from the surface by volatilization. According to Heinicke (2), a set of intermediate metal carbonyl sulfides are formed that lower the apparent activation energy of carbonyl formation. In either case, a very small amount of sulfur is required and excess sulfur hinders the reaction.

EXPERIMENTAL PROCEDURE

Chemical analysis of the chromite concentrates before reduction and carbonylation is summarized in table 1. The first three concentrates in the table are characterized as high iron because of the 1.5 to 1.7 Cr:Fe ratios, despite the 42.8 to 51.0 wt pct Cr_2O_3 they contain. The iron content of the fourth concentrate is not much greater than that of the first three, but because of the low Cr_2O_3 content, this concentrate has a 0.8 Cr:Fe ratio and is characterized as submarginal. The last chromite listed contains more Cr_2O_3 and less iron than the others, to give a 2.4 Cr:Fe ratio, and for this reason it is characterized as a high-chromium concentrate. Table 2 summarizes the particle size distribution for the five concentrates and shows that, except for the Montana high-iron, they fall into two groups: minus 100 plus 200 mesh and minus 200 mesh. The Montana high-iron concentrate consists of all three size fractions.

Since unreduced chromite will not react with CO under pressure to form metal carbonyls, the chromite samples were first subjected to a reduction roast in H_2 or CO. All of the reductions were solid-state reductions.

TABLE 1. - Characteristics of domestic chromite concentrates prior to reduction and carbonylation

Concentrate	Analysis, wt pct					Cr:Fe ratio
	Cr_2O_3	Fe	MgO	Al_2O_3	SiO_2	
Montana high-iron.....	42.9	18.7	11.8	16.9	1.3	1.6
Alaska high-iron.....	51.0	20.7	10.2	8.3	2.0	1.7
California high-iron.....	42.8	19.5	12.8	23.0	1.6	1.5
Alaska submarginal.....	26.3	22.6	15.1	23.0	2.0	.8
Alaska high-chromium.....	55.0	15.6	12.4	10.1	3.2	2.4

TABLE 2. - Particle size distribution of domestic chromite concentrates, weight percent

Concentrate	+100 mesh	-100, +200 mesh	-200 mesh
Montana high-iron.....	4.4	23.4	72.2
Alaska high-iron.....	0	100	0
California high-iron..	0	0	100
Alaska submarginal....	0	100	0
Alaska high-chromium..	0	100	0

Hydrogen reductions were made on 250- or 550-g concentrate charges in a high-temperature furnace from 1,100° to 1,235° C for periods from 4 to 16 h. The concentrates were heated from ambient temperature to 400° C under helium, from 400° C to roast temperature under H_2, held under H_2 at roast temperature for the set time, cooled to 400° C under H_2, and cooled to ambient temperature under helium. During reduction, a 2.4-SLM H_2 flow was maintained through the furnace. CO reduction was carried out on 25-g charges in a mullite tube heated by a small high-temperature tube furnace. Roast time was 20 h at 1,200° or 1,300° C under a 0.5-SLM CO flow. The charges were heated to 400° C under helium, from 400° C through roast back to 400° C or from 400° C through roast under CO, and then back to ambient temperature under helium.

Carbonylation tests were performed in stainless steel high-pressure reaction vessels. A 0.55-L reaction vessel was used with chromite samples weighing up to 40 g, and a 4.52-L reaction vessel was used with samples to scale up to 200 g. The reactors were encased in electrical heating jackets, and the temperature was measured by an iron-constantan thermocouple in a well attached to the inside of each reactor cap. Commercial CO was supplied through a high-pressure regulator, valves, tubing, and connections in the removable cap, and it exited through a metering valve in the reactor bottom or cap. Auxiliary connections and valves were attached to the inlet tubing to admit purge gases and promoters. Exit gas flow was measured by a precision bore rotameter downstream from the metering valve. No stirring or shaking mechanism was used. Figure 1 is a schematic drawing of the experimental carbonyl processing system.

Samples were inserted into the small reactor in fused silica boats and into the large reactor either in boats or directly. The reactors were maintained at temperature between experiments, and the charges were loaded into heated reactors. Following loading, the reactors were closed and purged with the desired gas before the promoter and CO were added. Duration of the purge could be varied, but it was at least long enough for the reactor temperature to stabilize. Test duration was measured from the time the reactor attained the test pressure to the time depressurization began. A nominal 0.15- or 0.30-SLM CO flow rate was maintained through the reactor to vapor-transport part of the iron pentacarbonyl from the reactor. The gases were passed at atmospheric pressure through a 3.0-cm-diam borosilicate tube maintained at

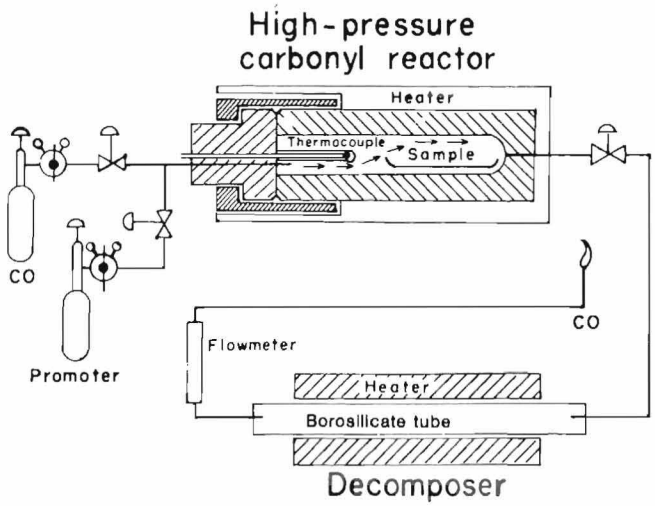

FIGURE 1. - Carbonyl processing system.

250° C in a 45-cm-long tube furnace. The iron pentacarbonyl decomposed in the hot zone back to CO and metallic iron, and the latter plated out on the borosilicate tube. All CO from the process was flared as a safety precaution.

The amount of iron extracted from the charge by carbonylation was calculated from charge weight loss and by chemical analysis of the residual charge. Total iron and chromium in the concentrates were determined by oxidation-reduction titration or by inductively coupled plasma emission spectrometry (ICP). Accessory mineral elements aluminum and magnesium were measured by atomic absorption, and silicon was measured by standard gravimetric methods. Since only reduced iron reacted with the CO, weight loss was used as a rapid means to establish the effectiveness of carbonyl treatment and chromite upgrading. The validity of this method was verified by chemical analysis of selected samples.

The initial carbonylation study consisted of a set of screening tests conducted on the Montana high-iron chromite concentrates at 1,200-psig CO pressure and 120° C, selected because of favorable carbonyl formation from reduced ilmenite (12). The influences of promoter, reaction duration, charge purge, chromite pretreatment, and charge size on carbonyl formation were investigated. Once these influences were defined, the effects of temperature, CO pressure, and promoter quantity were investigated in a response surface developmental experiment that tested three factors at three levels, in random order. This was followed by carbonylation at extrapolated points of promising data trends.

Finally, four other solid-state H_2- and CO-reduced domestic chromite concentrates were carbonylated at the optimum pressure, temperature, and promoter levels gleaned from developmental tests.

RESULTS AND DISCUSSION

CONCENTRATE PRETREATMENT

The parameters required for effective concentrate reductive pretreatment were investigated concurrently with the carbonylation screening and developmental tests. Montana high-iron concentrate was used to determine best temperature-time combination for solid-state H_2 reduction and to ascertain that CO could be utilized for the chromite concentrate reductive pretreatment. Results of the reduction studies are summarized in table 3.

The results show that during H_2 reduction the metallic fraction of the iron increases with temperature and duration of the roast, and after 16 h at 1,235° C, approximately 95 pct of the iron is metallic. CO roasts at 1,200° and 1,300° C (concentrates I and J, table 3) produced concentrates with 4.0 and 1.7 wt pct C, respectively, which hindered subsequent carbonyl formation. Carbon pickup from the reducing gas was eliminated by cooling the concentrates from roast temperature to ambient temperature under helium rather than cooling to 400° C under CO before changing to helium. The higher temperature CO roasts resulted in apparent complete reduction of the iron oxide fraction and possible reduction of chromic and accessory mineral oxides. This aspect was not pursued since our goal was to verify that CO reduction would render the concentrate amenable to carbonylation; subsequent CO reductions of the other chromite concentrates, listed in table 4, were performed under the same conditions as those for the last entry in table 3.

Table 4 summarizes H_2 and CO roasts on the chromite concentrates from Alaska and California. In all cases, the CO roast reduced all the iron oxides to metallic iron, whereas the H_2 roast did not. The higher degree of reduction under CO is attributed to the 100° C higher roast temperature. From the H_2 reduction data in table 3, it is evident that the degree of metallization can be controlled by the roast temperature and/or duration. The H_2 reduction data in table 4 imply that

TABLE 3. - Characteristics of Montana high-iron chromite concentrate after solid-state H_2 and CO reduction

(Heated to 400° C under He, 400° C through roast back to 400° C under reducing gas, and 400° C to ambient under He. H_2 reduction performed on 250-g charges and CO reduction on 25-g charges)

Reducing gas	Concentrate designation	Roast temperature, °C	Roast time, h	Analysis, wt pct			
				Cr_2O_3	Fe		C
					Total	Metallic	
None	A[1]	NAp	NAp	42.9	18.7	0	0.05
H_2	B	1,100	4	43.8	19.1	7.7	.02
	C	1,150	4	44.1	19.2	9.8	ND
	D	1,200	4	44.1	19.2	10.0	ND
	E	1,150	16	44.4	19.3	12.1	ND
	F	1,200	16	44.8	19.5	15.4	.01
	G[2]	1,200	16	44.6	19.4	13.7	ND
	H	1,235	16	45.2	19.7	18.7	.02
CO	I	1,200	20	43.0	18.8	15.1	4.0
	J	1,300	20	44.8	19.5	19.5	1.7
	K	[3]1,300	20	46.1	20.1	20.1	.05

NAp Not applicable. ND Not determined.
[1]Unreduced head sample. [2]550-g charge.
[3]Cooled from roast temperature to ambient under He.

TABLE 4. - Characteristics of chromite concentrate after solid-state reduction

(H_2 reduction--ambient to 400° C under He, 400° C through 16-h roast at 1,200° C and back to 400° C under H_2, 400° C to ambient under He. CO reduction--ambient to 400° C under He, 400° C through 20-h roast at 1,300° C under CO, 1,300° C to ambient under He)

Chromite concentrate and reducing agent	Analysis, wt pct			Cr:Fe ratio
	Cr_2O_3	Fe		
		Total	Metallic	
Alaska high-iron:				
None	51.0	20.7	0	1.7
H_2	54.1	22.0	21.4	1.7
CO	56.0	22.7	22.7	1.7
California high-iron:				
None	42.8	19.5	0	1.5
H_2	44.2	20.1	11.5	1.5
CO	45.8	20.9	20.9	1.5
Alaska submarginal:				
None	26.3	22.6	0	.8
H_2	28.2	24.2	24.2	.8
CO	28.9	24.9	24.9	.8
Alaska high-chromium:				
None	55.0	15.6	0	2.4
H_2	57.7	16.4	16.4	2.4

in addition to temperature and time, other parameters such as mineralogy and particle size govern metallization.

DESIGN SCREENING TESTS

Results of the experimental design screening tests at 1,200-psig CO pressure and 120° C temperature on four chromite concentrates characterized in table 3 are summarized in tables 5 to 10. Concentrate weight loss, Cr_2O_3 and iron content, iron extracted, and the Cr:Fe ratio are presented as functions of type and quantity of promoter, method of reactor purge, concentrate reduction, carbonylation time, and charge size, either singly or in selected combinations. Some of the data are repeated in the tables; this is done as an aid in depicting trends in the individual tables. Accessory mineral concentration is not shown in these tables (nor in table 11) because these oxides did not react with CO, although they would be concentrated slightly because of the iron loss from the bulk chromite concentrate.

The effect of H_2S promoter quantity on conversion of the iron to the carbonyl is summarized in table 5. The H_2S promoter was added as a one-time injection just prior to CO pressurization. In terms of concentrate Fe:H_2S mol ratio for 10-g charges, this amounts to a 4.3:1 ratio for the 0.008-mol-H_2S injection into the reactor. After CO pressurization, the corresponding CO:H_2S mol ratio was 171. Thus, while the mol quantity of H_2S in relation to contained iron is rather high, its low concentration in relation to CO limits its potential accumulation either by absorption or chemisorption on the reduced iron in the chromite concentrate or on the concentrate itself. This is borne out by chemical analysis, which showed that the reduced concentrates E and F contained <0.01 wt pct S before carbonylation and 0.3 to 0.4 wt pct S out of a maximum possible 2.5 wt pct after carbonylation promoted with the 0.008-mol-H_2S addition.

Data in table 5 show that H_2S definitely accelerates the carbonyl formation. Conversion of iron to the iron pentacarbonyl, as indicated by the charge weight loss and iron extraction percentages, shows 48- and 15-fold increases for the best cases for concentrates E and F, respectively. The highest H_2S promoter level shown indicates a decrease in

TABLE 5. - Dependence of iron extraction on promoter

(10-g charge, 1,200-psig CO pressure, 0.15-SLM CO flow, 120° C, 4-h duration, and He purge)

Concentrate[1]	Promoter		Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
	Type	Quantity, mol		Cr_2O_3	Fe		
E.....	None	0	0.18	44.6	19.2	0.9	1.6
	H_2S	.002	8.44	48.5	11.9	43.7	2.8
	H_2S	.004	8.16	48.3	12.1	42.6	2.7
	H_2S	.008	7.30	47.9	12.9	37.8	2.5
	H_2S	.011	6.87	47.7	13.6	35.2	2.4
	NH_3	.008	1.85	45.6	18.0	9.5	1.7
F.....	None	0	.68	45.1	18.9	3.5	1.6
	H_2S	.002	9.14	49.3	11.4	46.9	3.0
	H_2S	.004	10.01	49.8	10.5	51.3	3.2
	H_2S	.008	9.79	49.7	10.8	50.2	3.1
	COS	.008	5.44	47.4	14.9	27.9	2.2
	S[2]	.0006	7.74	48.6	12.7	39.7	2.6

[1]Designation from table 3.
[2]Elemental sulfur powder mixed with charge.

conversion, although conversion still is considerably higher than without any H_2S. In some tests where higher, but unknown, mol additions of H_2S than those shown in table 5 were used, conversion decreased further. This is in line with the reported decrease in iron conversion with excess sulfur (8) and results given later in this report in the section "Response Surface Developmental Tests."

The last entry for concentrate E and the last two entries for concentrate F in table 5 show that elemental sulfur, COS, and NH_3 also accelerate the carbonyl reaction. The gaseous promoters were injected in the same way as the H_2S, whereas the sulfur was mixed in powder form with the concentrate prior to insertion into the reactor. The quantity of elemental sulfur added was based on the residual sulfur found on H_2S-activated, carbonyl-treated concentrates. Observed iron conversions of the elemental-sulfur-activated carbonylations were more erratic than those of the gas-activated, and the value reported in table 5 is for the best case. No attempt was made to ascertain the optimum promoter-concentrate relationship.

Atmospheric oxygen was found to be deleterious to carbonyl formation with or without H_2S promoter, as demonstrated by the data in table 6. In all cases where the reactor was purged of atmospheric air with inert gases or by vacuum, carbonyl formation was observed. When the promoter and CO were injected directly over residual air or over purge air, no carbonyl formation was observed. The results imply that exposure of the reduced concentrate to the mixture of air and pressurized CO, rather than exposure of the concentrate to air prior to or during reactor loading, inhibits carbonyl formation. Usually 5 to 10 min lapsed between sample insertion and start of the reactor purge. Although the reduced concentrates were stored in sealed containers, they were frequently opened to air prior to use.

The need to reduce the chromite concentrate to render it amenable to carbonylation is shown by the data in table 7. The as-received chromite concentrate (A) was carbonylated both with and without promoter, and no weight loss was observed. Similar carbonyl treatment of the same material after H_2 reduction (E and F) resulted in iron conversion, especially when H_2S promoter was employed. In this phase of the study, only H_2 roast was used to reduce the iron oxides in the chromite concentrate to metallic iron. Since the primary requirement for carbonyl formation is that the iron be in

TABLE 6. - Dependence of iron extraction on method of reactor purge and H_2S promoter

(10-g charge of concentrate F, 1,200-psig CO pressure, 0.15-SLM CO flow, 120° C, 4-h duration, and 0.008 mol promoter)

Reactor purge	Promoter used	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
			Cr_2O_3	Fe		
He.....	No	0.68	45.1	18.9	3.5	1.6
	Yes	9.79	49.7	10.8	50.2	3.1
N_2.....	No	1.60	45.5	18.2	8.2	1.7
	Yes	9.92	49.7	10.6	50.9	3.2
Air.....	No	.21	44.9	19.3	1.0	1.6
	Yes	-.02	44.8	19.5	0	1.6
Vacuum.....	No	1.24	45.4	18.5	6.4	1.7
	Yes	10.42	50.0	10.1	53.4	3.4
CO_2.....	Yes	5.33	47.3	14.7	27.3	2.2

reduced state, chromite reduction by CO, natural gas, or other carbothermic methods would be acceptable. Results of carbonylation after CO reduction are given in the next section, "Response Surface Developmental Tests."

Tables 8 and 9 summarize iron carbonyl formation as a function of time. Data in table 8 show that most of the carbonylation with the H_2S promoter takes place during the first hour, in contrast to carbonylation without any promoter

TABLE 7. - Dependence of iron extraction on concentrate pretreatment and H_2S promoter

(10-g charge, 1,200-psig CO pressure, 0.15-SLM CO flow, 120° C, 4-h duration, 0.008 mol promoter, and He purge)

Concentrate[1]	Promoter used	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
			Cr_2O_3	Fe		
A.....	No	0	42.9	18.7	0	1.6
	Yes	0	42.9	18.7	0	1.6
E.....	No	.18	44.5	19.2	.9	1.6
	Yes	7.30	47.9	12.9	37.8	2.5
F.....	No	.68	45.1	18.9	3.5	1.6
	Yes	9.79	49.7	10.8	50.2	3.1

[1]Designation from table 3.

TABLE 8. - Dependence of iron extraction on carbonylation time

(10-g charge, 1,200-psig CO pressure, 0.15-SLM CO flow, 120° C, 0.008 mol H_2S promoter, and He purge)

Concentrate[1]	Carbonylation time, h	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
			Cr_2O_3	Fe		
C.....	1	5.36	46.6	14.6	27.9	2.2
	2	6.05	46.9	14.0	31.5	2.3
	4	5.36	46.6	14.6	27.9	2.2
	8	6.00	46.9	14.0	31.5	2.3
E.....	1	6.06	47.3	14.1	31.4	2.3
	4	7.30	47.9	12.9	37.8	2.5
	8	7.82	48.2	12.5	40.5	2.6

[1]Designation from table 3.

TABLE 9. - Iron extraction with long carbonylation times in the absence of promoter

(No promoter, no CO flow through reactor, 1,200-psig CO pressure, 120° C, and He purge)

Concentrate[1]	Carbonylation time, h	Charge weight, g	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
				Cr_2O_3	Fe		
E.....	91	4.8	8.74	48.7	11.6	45.3	2.9
F.....	70	1.0	11.41	50.6	9.1	58.5	3.8

[1]Designation from table 3.

(table 5) where even the 4-h iron conversion is an order of magnitude lower. In table 9, data are presented for extended-time carbonylation without promoter, which indicate that the carbonyl reaction will proceed without a promoter. The extended-time tests were made under static CO pressure on small samples to avoid a possible iron pentacarbonyl liquid-vapor equilibrium in the reactor. These data confirm the ability of a promoter, in this case H_2S, to greatly accelerate the carbonyl formation.

Carbonylation results on reduced chromite charges ranging in weight from 10 to 40 g are summarized in table 10. The maximum variation in weight here is only a factor of 4, and the data show no apparent influence of charge size on carbonyl formation. With large charges in a static bed, the diffusion of CO and iron pentacarbonyl away from the central region of the bed might be inhibited, but this was not detected in this phase of the study. Use of a fluidized bed or other means of charge agitation could be used to counter the reduced diffusion.

The series of tests at 1,200 psig CO and 120° C indicated that, of the variables studied, H_2S as a promoter had the greatest influence on accelerating and conceivably inhibiting the iron pentacarbonyl formation. The chromite concentrate had to be reduced and the reactor purged with an inert gas, or carbonylation would not occur; thus, these two variables easily defined the set condition that had to be met. Reaction duration in excess of 1 h and charge size did not have a marked influence on the iron conversion when a promoter was used.

RESPONSE SURFACE DEVELOPMENTAL TESTS

The effects of CO pressure, temperature, and H_2S promoter quantity on iron pentacarbonyl formation were investigated in a three-level, three-factor experiment on concentrate F. CO pressure was selected at the 600-, 1,200-, and 1,800-psig levels; temperature was 90°, 120°, and 170° C; and the amount of H_2S promoter added was none, 0.002, and 0.008 mol. A 2-h test duration was selected to best discern differences in carbonyl reaction acceleration. The chromite concentrate charge size was retained at 10 g, as was the 0.15-SLM flow of CO through the reactor. A helium purge calculated to equal at least 10 reactor volumes was made before the promoter was added and the reactor pressurized. One test was made at each of the 27 possible variable combinations, except that three repeat tests were also made at the three-variable center-point combination. All tests were made in a random sequence.

Figures 2 and 3 summarize the results at the 1,200- and 1,800-psig CO levels, respectively. Data at 600 psig CO are omitted because in no case did the charge weight loss exceed 3 pct, a very unfavorable value compared with that at the two higher pressures. Data points in figures 2 and 3 represent the test results, and

TABLE 10. - Dependence of iron extraction on charge size

(1,200-psig CO pressure, 0.15-SLM CO flow, 120° C, 4-h duration, H_2S promoter, and He purge)

Concentrate[1]	Charge weight, g	Promoter quantity, mol	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
				Cr_2O_3	Fe		
E.....	10.0	0.008	7.30	47.9	12.9	37.8	2.5
	15.0	.012	6.83	47.7	13.4	35.4	2.4
F.....	10.0	.008	9.79	49.7	10.8	50.2	3.1
	40.0	.032	10.09	49.8	10.5	51.7	3.2

[1]Designation from table 3.

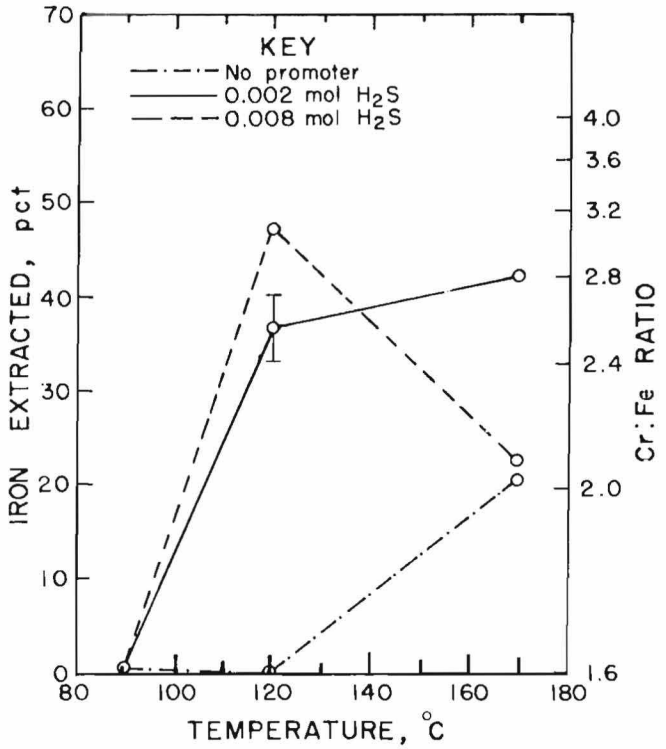

FIGURE 2. - Iron extraction as function of temperature and H_2S promoter at 1,200-psig CO pressure. Ten-gram charge of concentrate F, 0.15-SLM CO flow, 2-h duration, and He purge.

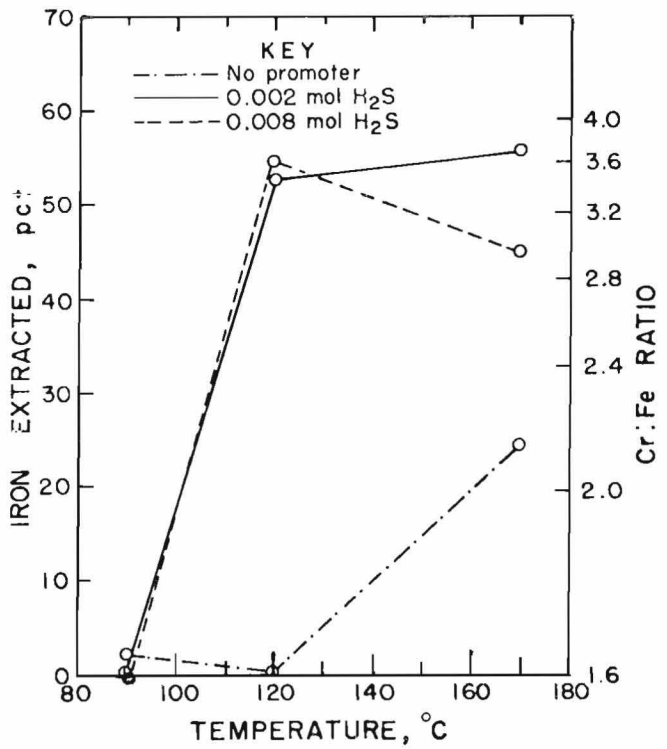

FIGURE 3. - Iron extraction as function of temperature and H_2S promoter at 1,800-psig CO pressure. Ten-gram charge of concentrate F, 0.15-SLM CO flow, 2-h duration, and He purge.

the lines between them indicate trends in iron conversion rather than predict values at intermediate temperatures. The vertical bar on the data point in figure 2 represents the standard deviation of the four tests made at the three-variable center-point value combination.

The results in figures 2 and 3 show no iron pentacarbonyl formation at 90° C at both CO pressures and at all three promoter levels. At 120° C, iron pentacarbonyl formation is still zero at both pressures without the promoter, but becomes pressure dependent as H_2S is added. The 0.008-mol addition produces the highest iron conversion in both cases. At 170° C, iron pentacarbonyl formation is still pressure dependent, but the promoter quantity roles are reversed compared with those at 120° C. The best conversion is achieved at the 0.002-mol-H_2S addition level; at the 0.008-mol level, conversion actually decreases markedly compared with that at 120° C. Also, at 170° C considerable iron pentacarbonyl formation is evident without any promoter. The pattern of carbonylation response at 600-psig CO pressure was similar to that at the two higher levels, except that significant carbonyl formation was observed only at the combination of 120° C and 0.008 mol H_2S promoter, where approximately 20 pct of the iron was extracted.

Based on the results shown in figures 2 and 3, tests were made at selected intermediate or extended temperatures and at one intermediate CO pressure to further define optimum iron conversion conditions. Figure 4 shows these results along with pertinent results at 120° and 170° C from figures 2 and 3. Optimum carbonyl formation is at 140° C for CO pressures of 1,200 psig and higher. At 120° C, the 0.008-mol-H_2S promoter addition produces higher iron conversion, but as the temperature increases, the 0.002-mol-H_2S addition becomes more effective

in accelerating the carbonyl reaction. Maximum chromite weight loss of 11.8 pct is realized at 1,500- and 1,800-psig CO pressure and 0.002 mol H_2S. The latter is equivalent to an Fe:H_2S mol ratio of 17:1. The resulting upgraded chromite concentrate contained 50.8 wt pct Cr_2O_3 and 8.7 wt pct Fe, had a 4:1 Cr:Fe ratio, and had 60.5 pct of the total iron extracted.

The decrease of iron conversion at the 0.008-mol-H_2S level with increasing temperature is attributed to increased H_2S chemisorption on the reduced iron in the concentrate and consequent formation of sulfide, which inhibits formation of iron pentacarbonyl. This is in agreement with the mechanism proposed by Queneau (8) for sulfide ion activation of an iron surface in carbonyl reactions.

Table 11 summarizes followup carbonylation tests on solid-state H_2- and CO-reduced Montana high-iron chromite concentrate performed at 1,500-psig CO pressure, 140° C, and 17:1 contained Fe:H_2S mol ratio. Concentrate H is the most highly H_2-reduced material and also shows the highest percent iron extracted for a 2-h period. Extending the carbonylation period to 24 h resulted in only 8 pct more iron extracted. The two 200-g charges were carbonylated in the large pressure reactor. The data here indicate a slower conversion rate in comparison with that for smaller charges during the 2-h treatment, which is attributed to possible charge packing. Concentrate K was prepared by CO reduction, and the data in table 11 show that its response to carbonylation is very similar to H_2-reduced concentrates in that the conversion is rapid and more than 50 pct of the iron is extracted.

Figure 5 shows four photomicrographs of the chromite concentrate. The as-received starting concentrate (*A*) has a predominantly smooth, gray reflectivity of the chromite in the polished-section photomicrograph. After H_2 reduction (*B*), metallic iron agglomeration is evident by the appearance of white specks and

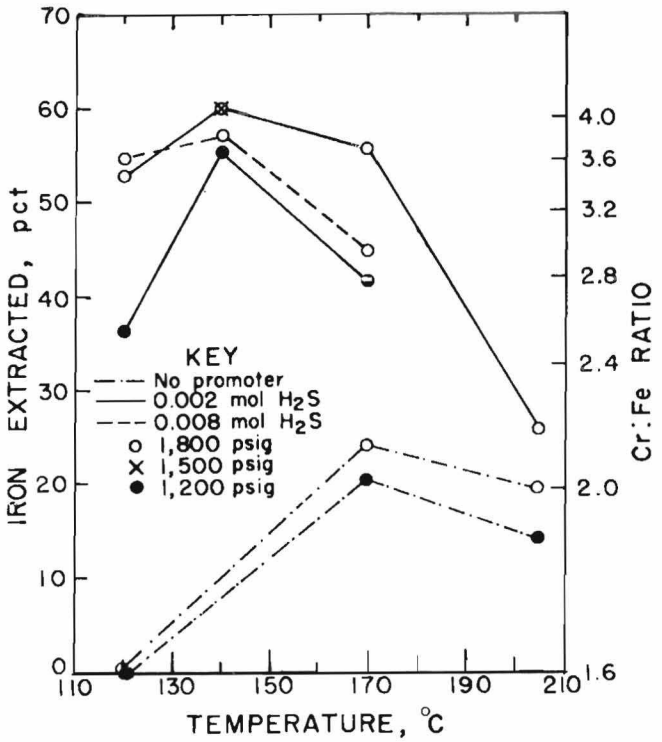

FIGURE 4. - Iron extraction as function of intermediate and extended temperature, intermediate pressure, and H_2S promoter. Ten-gram charge of concentrate F, 0.15-SLM CO flow, 2-h duration, and He purge.

coating on the periphery of the chromite grains in the photomicrograph, which disappeared after carbonyl treatment (*C*), leaving a residue of Cr_2O_3. The as-received carbonyl-treated concentrate (*D*) has the same appearance as the as-received material, indicating no carbonyl formation.

Photomicrographs of the same concentrate after CO reduction (*A*) followed by carbonylation (*B*) are shown in figure 6. Metallic iron agglomeration again is evident by the white specks along the periphery (*A*), which are less evident after carbonylation (*B*). The more noticeable agglomeration of the iron in the CO is attributed to the higher reducing temperature, and the presence of iron after carbonylation is in agreement with analysis that shows some iron remaining.

Iron pentacarbonyl vapor entrained in the CO flow through the reactor was

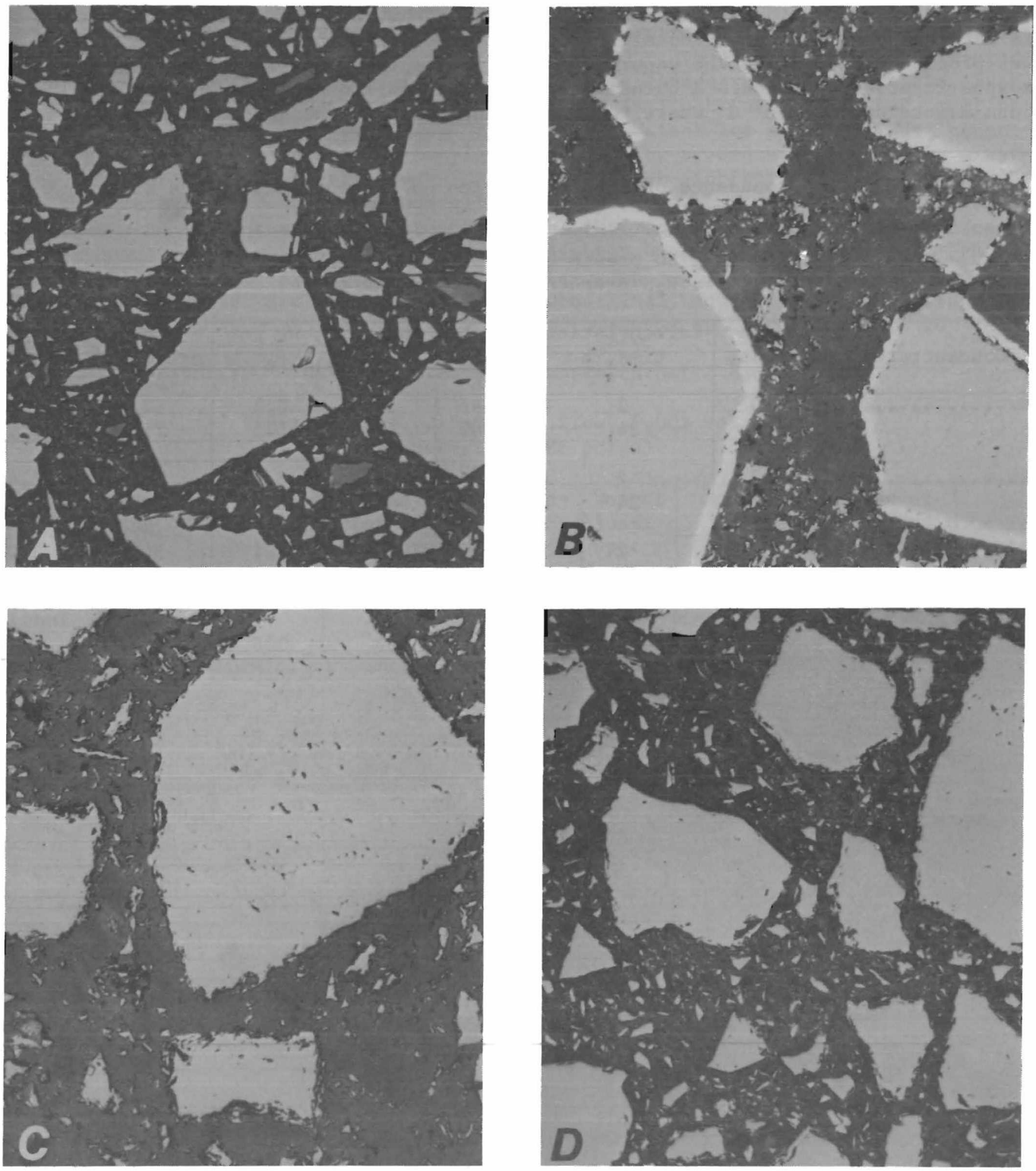

FIGURE 5. - Micrographs of Montana high-iron chromite concentrate (X 500). *A*, As-received concentrate shows a predominantly smooth, gray reflectivity of the chromite grains; *B*, after H_2 solid-state reduction, metallic iron is evident by appearance of white specks and coating along the periphery of the grains; *C*, the metallic iron has disappeared after carbonyl treatment, leaving a residue of Cr_2O_3; and *D*, the same chromite concentrate carbonylated without solid-state reduction shows no structure change.

recovered as a liquid by condensation or as metal by decomposition. Metallic iron was produced by passing the vapor at atmospheric pressure through a borosilicate tube maintained at 250° C where the iron plated out from the iron pentacarbonyl on the heated tube wall. Other methods of iron recovery are also feasible, and the recovered iron metal would be a valuable coproduct to the upgraded chromite.

TABLE 11. - Dependence of iron extraction on concentrate, charge size, and carbonylation time

(1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 17:1 Fe:H_2S promoter ratio, and He purge)

Concentrate[1]	Charge weight, g	Carbonylation time, h	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
				Cr_2O_3	Fe		
H.....	10	2	12.46	51.6	8.3	63.2	4.3
	10	24	14.09	52.6	6.5	71.5	5.5
G.....	200	2	6.95	47.9	13.4	35.8	2.4
	200	24	10.20	49.6	10.3	52.5	3.3
K.....	10	2	10.10	51.3	11.1	50.2	3.2
	10	24	11.65	52.2	9.6	58.0	3.7

[1]Designation from table 3.

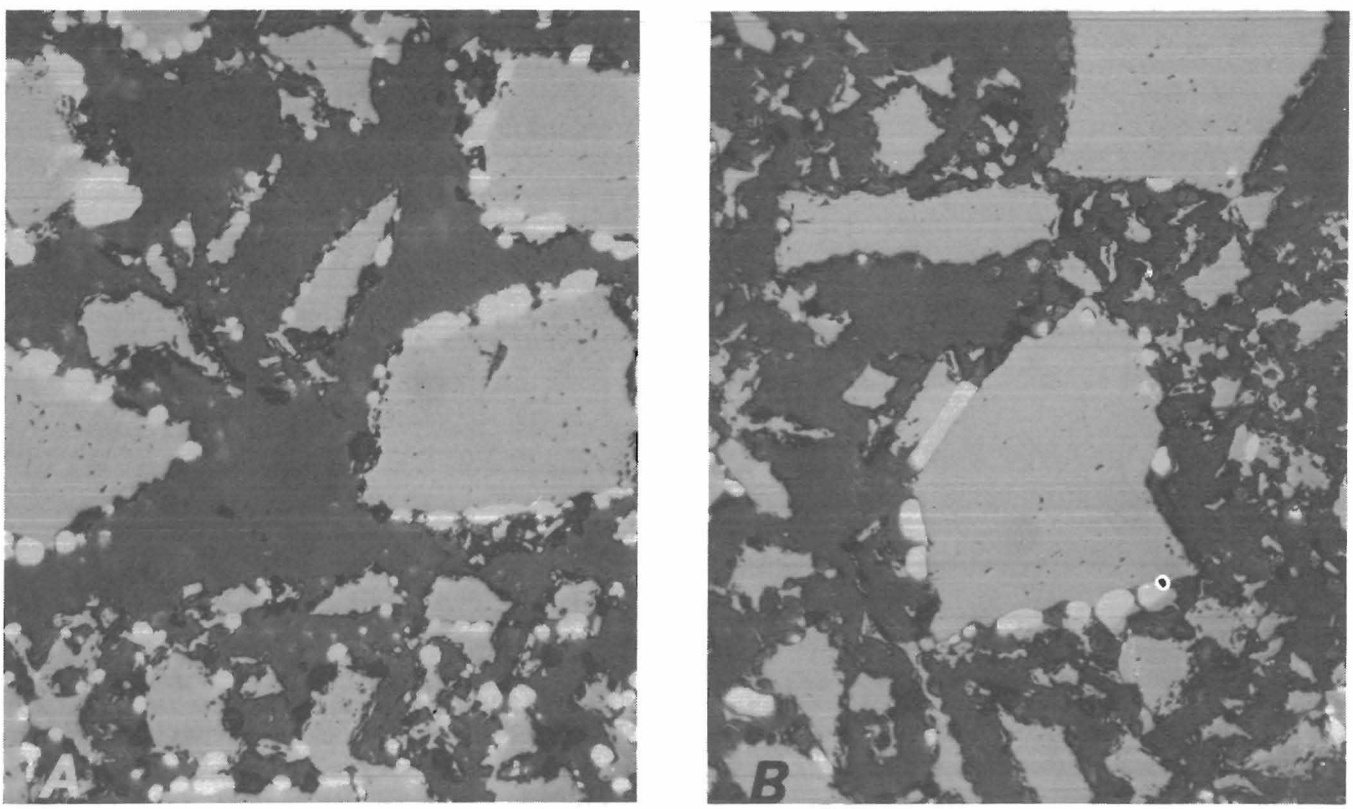

FIGURE 6. - Micrographs of CO-reduced Montana high-iron chromite concentrate (X 500). *A*, Metallic iron is evident as white specks along the periphery of the grains after CO solid-state reduction; and *B*, presence of metallic iron decreases markedly after carbonyl treatment.

CARBONYLATION OF OTHER DOMESTIC CHROMITE CONCENTRATES

The other four domestic chromite concentrates were also carbonyl-treated after solid-state H_2 or CO reduction to verify their responsiveness to carbonylation. All were found reactive with CO, with the best iron recoveries generally at the same pressure-temperature-promoter levels that produced optimum iron recovery from the Montana high-iron concentrate. The results are summarized in table 12.

From the standpoint of Cr:Fe ratios, all concentrates were upgraded to levels equivalent to or better than high-grade chromite concentrate, although the Alaska submarginal chromite did not meet the Cr_2O_3 content of a high-grade concentrate. The presence of accessory minerals did not inhibit the carbonyl upgrading process, but the fraction present in the upgraded concentrate increased slightly because of iron removal. Photomicrographs of the Alaska high-iron and submarginal concentrates following each processing step were similar to those

TABLE 12. - Carbonylation of domestic chromite concentrates

(10-g charge, 0.15-SLM CO flow, 0.002 mol H_2S promoter, and He purge)

Concentrate[1] and reducing agent	CO pressure, psig	Carbonylation temperature, °C	Carbonylation time, h	Weight loss, pct	Analysis, wt pct		Iron extracted, pct	Cr:Fe ratio
					Cr_2O_3	Fe		
Alaska high-iron:								
H_2.....	1,800	174	2	10.46	60.4	12.9	47.5	3.2
	1,800	140	2	11.32	61.0	12.0	51.5	3.5
	1,800	120	2	9.99	60.0	13.3	45.4	3.1
	1,500	140	2	7.28	58.3	15.9	33.1	2.5
CO.....	1,400	140	2	6.58	59.9	17.4	29.0	2.4
	1,400	140	24	11.87	63.5	12.3	52.3	3.5
California high-iron:								
H_2.....	1,800	140	2	4.81	46.4	16.1	23.9	2.0
	1,500	170	2	4.69	46.4	16.2	23.3	2.0
	1,500	140	2	4.98	46.5	15.9	24.8	2.0
	1,500	120	2	2.42	45.3	18.1	12.0	1.7
	1,500	140	24	6.47	47.3	14.6	32.2	2.2
CO.....	1,500	140	2	5.86	48.6	16.0	28.0	2.1
	1,500	140	24	10.02	50.9	12.1	47.9	2.9
Alaska submarginal:								
H_2.....	1,800	140	2	16.46	33.8	9.3	68.0	2.5
	1,500	140	2	16.45	33.8	9.3	68.0	2.5
CO.....	1,500	140	2	9.85	32.1	16.7	39.6	1.3
	1,500	140	24	15.20	34.1	11.4	61.0	2.0
Alaska high-chromium: H_2.	1,800	172	2	5.86	61.3	11.2	35.7	3.7
	1,800	145	2	7.01	62.0	10.1	42.7	4.2
	1,800	120	2	1.71	58.7	14.9	10.4	2.7
	1,500	140	2	4.86	60.6	12.1	29.6	3.4

[1]Analyses of unreduced samples shown in table 1.

of the Montana high-iron concentrate (figs. 5-6). The submarginal concentrate did exhibit iron agglomeration throughout the grains after reduction rather than agglomeration primarily on the periphery, but it is clear that this did not inhibit carbonyl formation because photomicrographs of the product showed that a series of voids had replaced the iron.

CONCLUSIONS

Laboratory tests have demonstrated that chromite concentrates can be upgraded by carbonyl processing. The concentrate must first be solid-state-reduced with H_2 or CO to convert the iron oxide fraction to metallic iron. Buildup of residual carbon must be avoided on the CO-reduced concentrates. The reduced iron in the concentrate readily reacts with CO to form the volatile iron pentacarbonyl, which is recovered as vapor or liquid, leaving a residual concentrate higher in Cr_2O_3 and with an increased Cr:Fe ratio. Carbonyl formation is accelerated markedly by small additions of H_2S as promoter and is poisoned by atmospheric oxygen. Optimum iron conversion is at 1,500-psig and higher CO pressures, 140° C, and at a contained Fe:H_2S mol ratio of 17:1. The iron pentacarbonyl is readily decomposed and the iron recovered as a coproduct with the upgraded chromite. The upgraded concentrate Cr_2O_3 level and Cr:Fe ratio are controlled by the degree of reduction in the precarbonylation roast, duration of the carbonylation treatment, and mineralogy of the starting concentrate. Cr_2O_3 content of the concentrate can be improved by as much as 10 pct and the Cr:Fe ratio increased up to three-fold compared with that of the starting concentrates.

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